

## **FOOD PACKAGE**

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### **CROSS REFERENCE TO RELATED APPLICATIONS**

This application claims priority to U.S. Provisional Application No. 60/391,099, filed June 24, 2002.

### **BACKGROUND OF THE INVENTION**

Plastic materials are used with increasing frequency to make packages for food and beverage products. The packages can take a wide variety of forms including bottles, canisters, tubs, films, wraps and bags. Thicker walled semi-rigid plastic is often used to make beverage containers. More rigid plastics with higher top load and hoop strength capacity are being used for heavier products or those requiring more durability through distribution such as through a warehouse system. Many numerous types of food and beverage products are available in plastic packaging.

The use of plastic has a ubiquitous presence in home food and beverage preparation and storage. Re-sealable containers in the forms of bags, tubs or trays provide a ready means of protection and containment. Thin, flexible continuous films are often used to wrap fresh or left over foods or to provide covering for storage containers.

A tradeoff with the use of plastic packaging with food and beverage products is the migration of unwanted constituents from the plastic package to the product. These constituents can contribute unwanted aromas or flavors that can be described as an off flavor. The off flavor imparted from the package can unfortunately predominate, leading to an objectionable taste and/or aroma experience for the consumer. Descriptors for a plastic off flavor can include terms like waxy, soapy, astringent, rubbery, and chemical. The off flavor is often associated with a coating sensation and a tactile feeling around the taste buds. The off flavor problem is made worse when present in lightly flavored products. These would include, but are not limited to water and snacks without added flavors such as plain potato or tortilla chips. Small packages can also be problematic since the ratio of package weight to stored product weight is often greater.

The occurrence of plastic off flavor has been observed to be worse when the package is stored at elevated temperatures such as about 85 to about 120°F (29 to 49 °C). A common

example is food prepared for a summer picnic such as a sandwich or snacks stored in a re-sealable plastic storage bag. Food when stored in this manner can acquire a plastic off flavor after only several hours of storage at an elevated temperature of between about 90°F (32°C) to about 100°F (38 °C), temperatures easily reachable during late spring, summer and early fall months, thus making the food less desirable. Package temperatures during shipping in North America can be above about 100°F (32°C) and can approach about 130°F (54 °C ) in tropical climates.

The level, display, and perception of plastic off flavor can be worse for products with a higher lipid content of about 10% or higher. Fried snacks such as potato chips, corn chips, or tortilla chips would be examples of snacks that have lipid contents from between about 24 to about 40%.

Increasingly, recycled plastics are being used in food and beverage packaging as a cost savings and ecological improvement measure. When the package itself is outside of its target weight or dimensions it is often rejected, then ground to a granular or flake consistency, then re-worked into a new package body. This is often done by combining the plastic re-grind with new virgin plastic resin. An alternate source of re-cycled plastic is obtained from including post consumer use material. The process of recycling plastic materials can lead to an increased presence of plastic off flavor.

The occurrence of plastic off flavor can be maddeningly random. It can be present at one time for a given plastic package unit under a given set of preparation and storage conditions, yet not be repeatedly present for an identical package prepared under seemingly similar conditions at an alternate time. The exact cause and effect between package making and the potential incidence of plastic off flavor has remained elusive. In turn, the achievement of a robust solution approach that consistently delivers plastic packaging for food and beverage products that is free of plastic off flavor has not appeared.

It would be advantageous to have food and beverage products delivered in plastic packaging without the presence of plastic off flavor and its deleterious effect on product acceptability. It would be of further benefit to have robust plastic packaging capable of consistently delivering plastic food or beverage products with no plastic off flavor through preparation and any storage or distribution scenario. It would be advantageous to have starting materials and methods capable of delivering said packaging or plastic surfaces that come in direct or in-direct contact with the food or beverage product. It would be advantageous to have methods for making the materials. Lastly, it would be advantageous to be able to use recycled

plastic materials within packaging for food or beverage products with no incidence of plastic off flavor.

### **SUMMARY OF THE INVENTION**

Accordingly the invention comprises a plastic comprising a level of detectable 8-Nonenal ranging from about 0 to about 400 ppt. Preferably, the plastic is substantially free of perceptible off flavor. Also, in one preferred execution the plastic is used to form a package (e.g., a food and/or beverage bearing package). Most preferably the package is constructed of a monolayer of plastic material. Typically, about 20 to about 100% of the package comprises from about 0 to about 1900 ppt of 8-Nonenal. Preferably, the level of said 8-Nonenal of a stored food or beverage product stored in the package for 7 days at a temperature of 150°F ranges from about 0 to about 400 ppt as measured in a grouping of representative packages with product therein.

The level of 8-Nonenal in plastic may be removed via various methods. For example, the 8-Nonenal level may be reduced in the plastic to range from about 0 to about 1800 ppt by stripping the 8-Nonenal from the plastic. Alternatively, the 8-Nonenal level may be reduced to range from about 0 to about 1900 ppt by the addition of anti-oxidants to the plastic. And still, the 8-Nonenal level may be reduced to range from about 0 to about 1800 ppt by limiting the metals content of colorants added to the plastic. Add to that that the 8-Nonenal level may be reduced to range from about 0 to about 1900 ppt by the addition of processing aids to the plastic material.

A package may be formed substantially from plastic, comprising the characteristics noted above; i.e., a package that is substantially free of perceptible off flavor. The package may comprise a multi-layer construction having an inside layer such that at least one of the layers comprise recycled plastic-- at least one the layers may form the inside layer of the package. In one embodiment herein at least one layer is separated from the inside layer by contact with at least one other package layer comprising plastic materials. In another preferred execution herein, the package may be constructed from a monolayer of plastic material.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

While the specification concludes with claims particularly pointing out and distinctly claiming the subject matter which is regarded as forming the present invention, it is believed that the invention will be better understood from the following descriptions which are taken in conjunction with the accompanying drawings in which like designations are used to designate substantially identical elements, and in which:

Figure 1 shows suitable fluidization curves for plastic particle size versus air velocity for a fluidized bed;

Figure 2 provides a two layer structure where the barrier layer is bonded directly to the substrate;

Figure 3 illustrates another embodiment where the barrier layer utilizes an adhesive tie layer to form the bond to the substrate;

Figure 4 shows another embodiment where the barrier layer is protected from degradation by an interior layer of either the same or a different substrate than is on the outside of the barrier layer;

Figure 5 shows another embodiment where the barrier layer is protected from degradation by an interior layer of either the same or a different substrate than is on the outside of the barrier layer; and

Figure 6 illustrates a layer sequencing that utilizes a recycle layer and two tie layers to bond the barrier layer to the adjacent layers.

#### **DETAILED DESCRIPTION OF THE INVENTION**

The term “plastic” refers to materials comprising polyolefins including, but not limited to (1) polyethylene, including, but not limited to, high density polyethylene, linear low density polyethylene, and ultra high molecular weight polyethylene, which contains one of the repeating units in a copolymer of the polyethylene monomer moiety, or blends of one or more other polymers. Those skilled in the art will appreciate and will know how to make the different types of copolymers that can be formed with polyethylene, including alternating block and graft copolymers as well as how to make the blends of polyethylene with other polymers; and (2) polypropylene, including homopolymers, copolymers which contain as one of the repeating units in a copolymer the polypropylene monomer variety, or blends of polypropylene and one or more other polymers. Those skilled in the art will appreciate and will know how to make the different types of copolymers that can be formed with polypropylene including alternating, block and graft copolymers as well as how to make blends of polypropylene with other polymers. Plastic materials also include polyvinyl chlorides, styrene polymers, including copolymers thereof, polyurethanes, nylons, polyesters, polycarbonate, polyacrylonitriles, vinyl alcohols and/or combinations thereof.

The term “product” refers to any food or beverage. The terms “package” or “packaging” are used interchangeably and are defined as any type of containment vessel that comes in direct or in-direct contact with a product stored inside wherein the term “direct contact” defines a

package surface that contacts the product. The term “in-direct” refers to a vessel that surround the headspace of the product and the interior surfaces are adjacent to the product, separated by a small distance.

The terms “off flavor” and “plastic off flavor” are used interchangeably and will refer to any flavor and/or aroma contributed by the package to the product that would produce product with a taste less preferred by a consumer than product that had not been stored in a plastic package.

The term “parts per million” will refer to the weight of a given material expressed in  $10^{-6}$  units, while the term “parts per billion” will refer to the weight of a given material expressed in  $10^{-9}$  units and the term “parts per trillion” will refer to the weight of a given material expressed in  $10^{-12}$  units.

The term lipid will be defined as any digestible or non-digestible shortening, oil, or emulsifier. Suitable lipids include, but are not limited to digestible, partially digestible, or non-digestible fats, oils, or emulsifiers that can be sourced from vegetable, animal or marine origins such as soybeans, corn, sunflower seeds, peanuts, cottonseed, tallow, lard, palm trees, or coconut.

Plastic off flavor was surprisingly identified during the course of this development to be caused by a single short chain aldehyde, 8-Nonenal at extremely low levels within the product. The 8-Nonenal is a nine carbon unsaturated aldehyde with a double bond between the eighth and ninth carbon atoms. It has a molecular weight of 140.2 grams/gram-mole. The 8-Nonenal contributed by the package to the product has a very low flavor threshold in the parts per trillion range. The 8-Nonenal can be measured in the product or package by first performing a water based simultaneous distillation and extraction of ground material, followed by a two dimensional gas chromatography separation that is subsequently and directly fed into a mass spectrometry detector. Alternately, a qualitative discovery for the presence of 8-Nonenal can be done using a Hewlett-Packard Model 6890 gas chromatograph with a Restek STABILWAX column that is 30 meters long, with an 0.23 millimeter inner diameter, and an 0.25 micron film thickness at a retention time of about 12 minutes and 30 seconds. A distinct odor that smells like a melted polyethylene bag can be observed.

The problem of plastic off flavor occurs due to three sets of circumstances. The first is that the source reactant materials needed to make 8-Nonenal are present during the plastic resin making process. The resulting resin contains 8-Nonenal and additional reactants to make more 8-Nonenal. The second circumstance is that the conditions for both resin and package making

enable 8-Nonenal formation on a relatively short time scale. For example, the total level of 8-Nonenal can increase several fold within 30 to 60 seconds of residence time experienced in some extruded plastic operations. Lastly, the diffusion of 8-Nonenal from package to product is governed by thermodynamic forces that lead to ready absorption of 8-Nonenal by the product. The occurrence of plastic off flavor is inevitable due to the controlling chemistry and physics that favor this outcome.

The source resin materials for plastic packaging contain low levels of unsaturated hydrocarbons, at levels up to about several hundred parts per million, that become the source materials for 8-Nonenal formation. The 8-Nonenal forms from an oxidation of unsaturated hydrocarbons present within plastic. The oxidation can be promoted by the presence of the unsaturated hydrocarbon source compounds, oxygen, and/or catalysts such as trace levels of divalent metals such as copper or ferrous iron. The oxidation reaction rate of these materials increases directly with increasing temperature. Examples of these hydrocarbons include, but are not limited to decene, 1-decene, dodecene, and tetradecene.

Oxidation can occur in the plastic forming process itself. The process of making plastic packaging often involves high heat exposure. Package forming processes such as injection molding, blow molding, or thermo forming all rely on using plastic in a melted, flowable state in order to achieve the desired shape formation flexibility. Extrusion of the plastic materials with single or twin screw extrusion machines is common. The frictional heat provided by contact interference with the screws melts the plastic and causes it to flow. Temperatures ranging from about 320°F to about 440°F or higher (160 to 227°C) have been observed. These temperatures are sufficient to drive the oxidation reaction. Additionally, exposure to air during the heating process is common, providing an abundant oxygen source that is readily incorporated within the plastic. The mixing that occurs when the plastic is formed increases the interfacial surface contact area between the hot melt plastic and oxygen leading to further acceleration of the reaction.

Thus, the conditions during plastic package making are ideal for the formation of 8-Nonenal and thus the production of plastic off flavor. Therefore, a difficult tradeoff can occur where running the process at conditions necessary to eliminate plastic off flavor may produce undesirable package attributes like improved shape and weight. Alternately, a severe decrease in production rate, e.g., to restrict conditions for oxidation, is not economically feasible or desired to deliver all of the flavor and other package attributes needed. Knowledge of package 8-

Nonenal levels provides for an organized process optimization approach, avoiding costly random trial and error methods.

During the course of this development, it has been ascertained that trace metals in the low part per billion range can greatly accelerate the oxidation reaction resulting in increased 8-Nonenal formation. These metals can be contributed by the package making process equipment or from additives such as colorants. The 8-Nonenal molecule is incorporated within the product by diffusion from the plastic package. At room temperatures of between about 70 to about 80°F (21 to 27°C), the 8-Nonenal is in an entrapped liquid form within the solid plastic matrix of the package. Thermodynamics favors the diffusion of 8-Nonenal from the package to the product. A three step mechanism involves movement of 8-Nonenal to the packaging surfaces, movement of 8-Nonenal to the product, and finally unabated accumulation and retention of 8-Nonenal which leads to 8-Nonenal incorporation within the product. The liquid 8-Nonenal will seek to reach an equilibrium concentration throughout the plastic. Some 8-Nonenal will reside at the surface of the plastic adjacent to product as a result of this drive towards an equilibrium concentration. When the food product directly contacts the package, the 8-Nonenal can directly diffuse into the product, especially lipid-containing products of relatively high lipid concentrations. When the contact is indirect, such as when there is a gas phase headspace around the product, the 8-Nonenal at the surface of the package will seek to reach phase equilibrium where some of the 8-Nonenal will continue to reside as a liquid within the plastic matrix while some is converted into a vapor within the headspace. The 8-Nonenal diffuses from the headspace to recondense within the product. The 8-Nonenal molecule is more soluble in the packaged product than in the plastic polymer package matrix enabling ready migration and partitioning into the product. The fact that it will take a much higher concentration of 8-Nonenal to saturate the product than the plastic, sets up an equilibrium imbalance that will cause the product to continuously draw 8-Nonenal from the package; the product becomes a sink with the capacity to eventually absorb all of the 8-Nonenal from the package.

A wicking type action is generated where 8-Nonenal is continually drawn to the inside wall surface from the wall interior as the plastic attempts to maintain an equilibrium concentration of 8-Nonenal throughout the thickness of the wall. The combination of a concentration gradient and the higher sorption isotherm for the product, where it will take a much higher level of 8-Nonenal to saturate the product than the plastic matrix, provides a large driving force for 8-Nonenal transport. The transport will be concentration dependent wherein higher levels in the plastic will increase the driving force and rate of accumulation in the product. Thus,

the incorporation of 8-Nonenal within the product from typical packaging is inevitable. Direct or intimate contact will increase the rate of diffusion such as when the product touches the interior wall of the package. Food products stored in flexible film packaging or beverages that by default flow to the package walls are two examples of this scenario.

Increased package storage temperatures will increase the rate of diffusion. At elevated temperatures the equilibrium vapor pressure of the 8-Nonenal in the package headspace will be higher, relating directly to a higher concentration of 8-Nonenal in the headspace. The porosity of the plastic structure will also increase, resulting in less resistance to 8-Nonenal flow to the package surface. The capacity for the product to absorb 8-Nonenal will also increase as the sorption isotherm shifts lower. All of these factors contribute to an increased rate of 8-Nonenal accumulation within the product with increased temperature.

Food products containing lipids will more readily display the 8-Nonenal plastic off flavor than foods with little or no lipids. The lipid phase is more physically like the 8-Nonenal molecule than other large molecule food components such as carbohydrates or proteins creating further partitioning driving forces that favor retention of the 8-Nonenal within the lipid phase. The 8-Nonenal molecule is mobile within the lipid phase leading to a more rapid concentration equilibration across the food product. The 8-Nonenal molecule is more readily removed from the edge towards the interior of the food. This effectively increases the driving force for the 8-Nonenal molecule to transport it to the food product. The increased mobility of the 8-Nonenal molecule also causes it to be more readily displayed because it increases off flavor perception. The subject of flavor partitioning from plastic packaging is reviewed in Lau, O.W. and Wong, S.K., "Contamination in Food from Packaging Material", *Journal of Chromatography A*, 882 (2000) 255-270.

The molecularly driven transport mechanism makes it difficult to make lipid containing foods in plastic packaging that do not incur a perceptible plastic off flavor. Preferably, the discoveries derived from this development are applied to food products with lipid contents of at least about 10, foods having lipid contents of preferably between about 15 to about 50%, more preferably from between about 20 to about 45%, and most preferably from about 25 to about 40%. A list of food products that would benefit from the present development can be found in U.S. Patent No. 5,306,515. The types of food products are preferably baked or fried products where the lipid is incorporated by mixing or absorption. These foods can include, but are not limited to baked or confectionary goods such as breads, cookies, crackers, muffins, chocolates,



candies or fried foods such as salted snacks, french fries, or doughnuts. Exemplary foods include fried salted snacks derived from farinaceous or vegetable based grains or tubers. Other food products for use with the packaging herein include potato chips, potato crisps, corn chips, tortilla chips, or expanded corn snacks such as puffs or twists.

Limiting the 8-Nonenal level in the product will reduce or eliminate the presence of plastic off flavor. The 8-Nonenal molecules will diffuse over time from the package to the product eventually leading to an unacceptable off flavor. A two month old shelf life or longer from the time a product is packed until it is consumed is typical for many food and beverage products. It would be desirable for the product to have no plastic off flavor during 2 months of storage, preferably for about 5 months of storage, more preferably for about 9 months of storage, much more preferably for about 12 months of storage, and most preferably for about 18 months of storage. To avoid plastic off flavor perceptions the level of 8-Nonenal should range from about 0 and extend to about 450 parts per trillion (ppt) in the product, or preferably from about 0 to about 300 ppt, or more preferably from about 0 to about 200 ppt, much more preferably from about 0 to about 100 ppt, and most preferably between about 0 to about 50 ppt. The total level of 8-Nonenal contained in the product (e.g., lipid-containing snacks) should range from about 0 to about 700 ppt, preferably from about 0 to about 550 ppt, more preferably from about 0 to about 450 ppt, much more preferably between about 0 to about 400 ppt, and most preferably from about 0 to about 300 ppt.

The delivery of consistent product performance with no plastic off flavor perception is a benefit to the end consumer. Preferably the average stored product temperature while packed in the plastic package is been between about 65 to about 85°F. After about 45 to about 60 days of storage the percentage of product that has an 8-Nonenal level ranging from between about 0 to about 200 ppt should be between about 0 to about 95%, preferably between about 0 to about 75%, more preferably between about 0 to about 50%, much more preferably between about 0 to about 25%, and most preferably between about 0 to about 15%. Preferably the percentage of product with an 8-Nonenal level of less than 150 ppt after about 45 to about 60 days of storage is between about 5 to about 100%, more preferably between about 25 to about 100%, much more preferably between about 50 to about 100%, and most preferably between about 75 to about 100%. After about 120 to about 150 days of storage the percentage of product that has an 8-Nonenal level of between about 0 to about 450 ppt should be between about 0 to about 95%, preferably between about 0 to about 75%, more preferably between about 0 to about 50%, much more preferably between about 0 to about 25%, and most preferably between about 0 to about

15%. Preferably the percentage of product with an 8-Nonenal level of less than 350 ppt after about 120 to about 150 days of storage is between about 5 to about 100%, more preferably between about 25 to about 100%, much more preferably between about 50 to about 100%, and most preferably between about 75 to about 100%. Herein, the term "percentage of product" refers to the percentage of representative packages containing product. As an example, at least twenty packages containing product representative of one or more production cycles should be used for measurement.

Limiting the 8-Nonenal level within the plastic package is one means of preventing diffusion of plastic off flavor from the package to the product. The level of 8-Nonenal in the package should range from between about 0 to about 1900 ppt, preferably between about 0 to about 1500 ppt, more preferably between about 0 to about 1000 ppt, and most preferably between about 0 to about 300 ppt. Since the size of the package relative to the amount of product stored can effect the amount of 8-Nonenal diffusion to the product, it is useful to define a ratio of the total weight of 8-Nonenal in the package to the weight of product. Preferably, the measurement of package 8-Nonenal should be made within about 7 days of product being packaged, more preferably within about 3 days to minimize the amount of diffusion between the package to the product. Preferably the product is stored in the package at a temperature between about 65 to about 85°F on average. The ratio of the weight of 8-Nonenal in the package to the weight of product should be from about 0 to about  $5.27 \times 10^{-10}$ , preferably from about 0 to about  $4.12 \times 10^{-10}$ , more preferably from about 0 to about  $3.88 \times 10^{-10}$ , more preferably from about 0 to about  $2.78 \times 10^{-10}$ , much more preferably between about 0 to about  $1.94 \times 10^{-10}$  and most preferably from about 0 to about  $1.39 \times 10^{-10}$ .

Ideally the diffusion rate of the 8-Nonenal molecule from the package to the product is low. In one instance herein, a lower initial 8-Nonenal concentration will slow the rate of diffusion through the package. Absorbents can be admixed with the plastic material or a barrier material can be placed between the interior plastic surface of the package and the product to slow the rate of diffusion. The amount of diffusion can be expressed as a percentage of the starting 8-Nonenal level in the package that has diffused to the product. This can be calculated by subtracting the weight of 8-Nonenal that has diffused to the product over a given time period from the starting weight of 8-Nonenal in the package and dividing the result by the starting weight of 8-Nonenal in the package. The average amount of diffusion is calculated by dividing the total amount of diffusion by the months of storage where a month is defined as a 30 day period in length.

The amount of diffusion will also be temperature dependent. At a storage temperature from about 70 to about 80°F the average amount of diffusion should range from between about 0 to about 5.5% per each month of storage, preferably from about 0 to about 4.1% per each month of storage, more preferably from about 0 to about 2.9% per each month of storage, and most preferably from about 0 to about 1.2% per each month of storage. At a storage temperature from about 85 to about 95°F the average amount of diffusion should be from about 0 to about 10% per each month of storage, preferably from about 0 to about 7% per each month of storage, more preferably from about 0 to about 5% per each month of storage, and most preferably from about 0 to about 2.5% per each month of storage. At a storage temperature from about 100 to about 120°F the average amount of diffusion should be from about 0 to about 15% per each month of storage, preferably from about 0 to about 12% per each month of storage, more preferably from about 0 to about 8% per each month of storage, and most preferably from about 0 to about 4% per each month of storage.

There are several approaches towards limiting the presence of 8-Nonenal within plastic packages and the products stored within them. Limiting the oxidation of the plastic material will hinder the rate of 8-Nonenal formation. Entrapping the 8-Nonenal within the plastic matrix can also be an effective means of control. The 8-Nonenal can also be removed from the starting materials, in-process materials, or from the final package.

The use and control of additives in the making of plastic packaging can reduce the formation of 8-Nonenal within the package. The purpose of these additives is to limit the rate of the oxidation reaction.

Antioxidants are commonly used within the plastics industry as a source of aroma improvement. Primary and secondary antioxidants can both be effective. The primary antioxidants can include, but not be limited to phenolid compounds, hindered phenols and hindered aromatics. The secondary anti-oxidants can include, but are not to be limited to peroxide decomposers such as phosphite and thioester compounds. Antioxidants can be used singularly or in combination. A review on the functionality of anti-oxidants in plastic applications can be found in "Quantitative Analysis of Antioxidants from High Density Polyethylene (HDPE) by off-line Supercritical Fluid Extraction Coupled with High Performance Liquid Chromatography", a Master of Science thesis published by Angela M. Pinto, Virginia Polytechnic Institute, 1997, pages 1-8. Other review articles include 'Stabilization of Polyolefin Compounds for Wire & Cable Applications', Neri et al., presented at the American Chemical Society-Rubber Division Wire & Cable Conference, 2001 and "Effect of Resin Types and

Antioxidants on Release of Off-flavor from HDPE Bottles", Yam et al., Polymer-Plastic Technology Engineering, 35(5), 727-755, 1996.

Sufficient antioxidant needs to be added to the plastic mixture to minimize 8-Nonenal formation, but preferably not so high as to be above the saturation level of the plastic and not be soluble. Antioxidants with different compositions can be combined to provide a synergistic effect. For example, it is commonly known that combining primary and secondary antioxidants can renew the effectiveness of the primary antioxidant. The total level of antioxidant expressed as a percentage of the total weight of plastic materials and antioxidant should be between about 0.08 to about 5.0%, preferably from about 0.10 to about 2.0, more preferably from about 0.15 to about 1.0%. When using primary phenolic based antioxidants the level of antioxidant should be from about 0.06 to about 5.0%, preferably from about 0.10 to about 2.0%, more preferably from about 0.15 to about 1.0%, and much more preferably from about 0.15 to about 0.50%, and most preferably from about 0.15 to about 0.30% where the antioxidant is expressed as the percentage of total weight of the combined plastic and antioxidant mixture. When using a secondary phosphite based antioxidant the level of antioxidant should range from between about 0.02 to about 2.0%, preferably from about 0.10 to about 1.0%, more preferably from about 0.10 to about 0.50%, and most preferably from about 0.10 to about 0.20%. When both primary and secondary antioxidants are used the weight ratio primary to secondary antioxidant should range between about 5:1 to about 0.6:1, preferably from about 2:1 to about 0.8:1, more preferably from about 1.5:1 to about 1:1, and most preferably from about 1.2:1 to about 1:1.

Frequently the processing temperatures of the plastic melt need to be high on the order of 380 to 420°F (193 to 216°C) or higher in order to achieve the flow characteristics that best deliver the desired package shape. This in turn leads to heat stress and further oxidation of the plastic. Decreasing the processing temperature of plastics allows for decreased degradation during heating. A wide variety of additives can be used to decrease the processing temperature. Additives can include but are not limited to processing aids, flow aids, and lubricants. These additives can be made of but not limited to small molecules and high-molecular weight polymers which effectively reduce the apparent shear stress and viscosity on the resin causing less heat generation from shear and decreased flow temperature allowing adequate flow at lower temperatures. By lowering the processing temperature oxidation of the plastic is reduced which causes lower 8-Nonenal generation. Exemplary processing aids include but are not limited to methyl methacrylate, alkyd acrylates, ethyl acrylates and butyl acrylates. Most preferably Dynamar PPA FX 5911X made by Minnesota Mining and Manufacturing Corporation of

Minneapolis, MN would be used in food or beverage applications where HDPE is the packaging material. Alternate processing aids that increase the flow properties of the plastic can be found in U.S. Patent No. 4,564,658, U.S. Patent No. 5,280,060, U.S. Patent No. 5,710,217, World Intellectual Property Organization Patent Application WO0194460A3, World Intellectual Property Organization Patent Application WO0226875A1, World Intellectual Property Organization 02/0783 A1, and U.S. Patent No. 6,380,313. Additives that suppress the processing temperature would be beneficial during heating of virgin material and subsequent heating of plastic material that is recycled from the plastic production such as the collection, grinding, and reintroduction of the blow pockets from a blow molding operation.

Commonly found impurities include but are not limited to potassium, manganese, calcium, iron, sodium, magnesium, phosphorus, zinc, copper, and nickel. It is known to someone skilled in the art that metal ions of but not limited to iron, copper, zinc, and nickel can act as oxidation catalysts when present in the correct valence and is well documented.

In the present development, metal ions have been determined to catalyze oxidation of plastic and therefore the formation of 8-Nonenal. For example, TiO<sub>2</sub> (white colorant) is produced from ores containing these ions, which are then found as impurities in TiO<sub>2</sub> as such results in catalytic oxidation of polyolefin materials. Preferably, colorants and additives would have low levels of total metal ion content below about 1 part per million, more preferable below about 100 part per billion, even more preferably below 10 part per billion, and most preferably below 1 part per billion.

The removal or stabilization of metals in pigments such as titanium dioxide or calcium carbonate can be found in U.S. Patent No. 3,679,721, U.S. Patent No. 4,066,610, U.S. Patent No. 5,690,897, European Patent Application EPO785250A1, and European Patent Application EPO1052225A1. Plastic additives effective at reducing metal catalyzed oxidation applicable to the present development including selective antioxidants and alkyl groups can be found in U.S. Patent No. 3,931,103 and U.S. Patent No. 4,963,605. Ideal chelation agents comprise an unshared electron pair that can form a complex with metal ions rendering unable to promote oxidation. Organic acids that provide a chelation effect can be added such as, but not limited to citric, ascorbic, malic, ascorbic, or phosphoric acids. These acids should be added between about 20 to about 300 ppm, preferably between about 50 to about 200 ppm. Alternately, polyphosphates or ethylenediaminetetraacetic acid (EDTA) can be added as chelating agents.

Lowering the 8-Nonenal level in the starting plastic resin material can contribute to lower 8-Nonenal levels in the final package. The 8-Nonenal levels in starting resin should be

between about 0 to about 450 ppt, preferably between about 0 to about 300 ppt, more preferably between about 0 to about 150 ppt, and most preferably between about 0 to about 50 ppt. Lower 8-Nonenal levels in the starting resin can be produced by lowering the process temperature; blanketing the raw materials, process and final resin in a low to non-oxygen atmosphere by using inert gasses such as nitrogen or argon; the addition of primary and/or secondary antioxidants; and the addition of metal chelating agents. Alternately, 8-Nonenal can be removed from the final resin. Methods of removal can include, but are not limited to extraction, stripping including aqueous washing or convective evaporation with air, and distillation.

Limiting the diffusion of the 8-Nonenal from the package to the product is an alternate approach for preserving the product flavor. One method for limiting diffusion is to add an absorbent to the plastic matrix that is capable of entrapping the 8-Nonenal molecule within the plastic matrix. These absorbents can include, but are not limited to crystalline siliceous molecular sieves such as zeolites and cyclodextrins. Suitable molecular sieve compositions can be found in U.S. Patent No. 5,750,611 and "Identification of Off-Flavor Compounds in High-Density Polyethylene (HDPE) With Different Amounts of Abscents", Polymer Engineering and Science, June 1998, Vol. 38, No. 6922-925 by Villberg, K. and Veijanen, A.. Suitable cyclodextrin compositions can be found in U.S. Patent No. 6,136,354.

Plastic packages can be either mono-layer or multi-layer in order to meet the necessary performance requirements. Often it is desirable to incorporate recycled material into the package to minimize scrap and material costs. Regrind (i.e., ground, recycled plastic) is often incorporated back into the package in a specific layer or layers known commonly as the regrind layer. The regrind source can often be material trimmed from the final package such as blow pockets or packages that do not meet specifications which are then returned to the raw material stream to be converted to regrind and reworked into packages with acceptable specifications. Two problems arise with the practice of using regrind or recycled materials. The first is that the plastic experience repetitive heat and oxygen exposure, promoting increased 8-Nonenal levels. The second is that minor components, like colorants and their inherent divalent metal composition, are incorporated within the regrind and recycled plastic resulting in further 8-Nonenal formation. One solution would be to limit package composition to only virgin plastic materials that have experienced a single heat processing cycle during package making. While this will lead to lower 8-Nonenal levels, it is not economically practical since large amounts of excess waste plastic material will be developed. The amount of this waste material can approach about 30 to 50% of the total materials used. Thus, it would be desirable to be able to use regrind

and recycled plastic materials with no or at least limited increased potential for 8-Nonenal formation.

The regrind layer can either be exposed on a surface or exist as an inner layer surrounded by other layers. This regrind layer can be up to 100% regrind, however, this layer often contains some amount of virgin material to control dissimilarity between the regrind and virgin layers and maintain adequate bonding between layers to prevent delamination. To maintain bonding between 15 and 95% virgin material should be added to the regrind layer. Preferably the regrind layer should contain greater than about 25% virgin material, more preferably than about 40% virgin material and most preferably than about 60 %virgin material. The blend of virgin and regrind plastic materials to make an improved regrind layer can be found in U.S. Patent No. 4,894,291.

The quality of regrind can influence both where the layer should go in the package and how much should be present in a regrind layer. In practice, preferred regrind treatment requires that it be kept as cleanly as possible to prevent it from picking up any and all impurities; e.g., grease, dirt, air-borne particles metal, etc. Impurities can cause processing problems and could catalyze oxidation during reprocessing. The 8-Nonenal concentration in the regrind or recycled plastic should be between about 0 to about 2000 ppt, preferably between about 0 to about 1500 ppt, more preferably between about 0 to about 1000 ppt, much more preferably between about 0 to 500 ppt, and most preferably between about 0 to about 300 ppt. The levels of 8-Nonenal in the regrind or recycled plastic can be reduced by methods previously disclosed such as the use of antioxidants, controlling divalent metals contamination, or the addition of chelation agents.

To free polyolefin materials from undesirable substances (e.g., 8-Nonenal), heat may be used to increase the diffusion rate of atoms or compounds by providing the necessary activation energy for diffusion through a material, thus moving the undesirable materials out of the polyolefin materials. Heating temperatures can range from between about 100°F to 350°F (38 to 177°C) depending on the material composition. Preferably the temperature would be below the softening temperature of the plastic. Heat exposure preferably would be greater than about 15 and less than about 600 minutes, more preferably greater than about 30 minutes and less than about 400 minutes, and most preferably greater than 60 minutes and less than about 180 minutes. The diffusion rate out of the material can be increased further by increasing the surface area and decreasing the diffusion distance within the material itself such as by grinding the material into a flake, granular or powder consistency.

To remove the volatilized compounds the material can move through a fluid. A fluid low in volatiles is preferred to not limit the removal of the compounds to keep the compound content in the fluid well below the solubility limit. Preferably, the fluid is clean, dry air. A dryer is commonly used in plastics to remove moisture from plastic resin before it is processed if the plastics' properties are adversely affected by moisture. For example, PET is typically dried before being processed in order to maintain tensile strength. Dryers are a preferred means to remove compounds from plastics. A more preferred method would be a fluidized bed where the materials are heated by heated air that is blown through a vessel containing the materials. Figure 1 shows suitable fluidization curves for plastic particle size versus air velocity for a fluidized bed. This process could be done in either a batch or continuous operation. A preferred embodiment of method may be a means by which the incoming plastic resin is treated using a continuous dryer. A more preferred embodiment is the process in which recycled material is treated in a continuous fluidized bed before being reintroduced into the package. A most preferred method may be to treat select recycle material that has been segregated from the majority of recycle because it is high in aldehydes. Suitable dryers or fluidized bed processes applicable to the current development can be found in U.S. Patent 5,199,184 [Rosse, 1993], European Patent Application EP549577A1 [Wolf, 1993], World Intellectual Property Organization Patent Application WO9514201A1 [Jackwitz et al., 1995], European Patent Application EP0937557A1 [Kunieda et al., 1999], U.S. Patent 5,867,921 [Maruyama and Matsuska, 1999], and U.S. Patent 6,298,579 [Ichitani et al., 2001]. A further survey of processes applicable to the present development to remove 8-Nonenal by evaporation can be found in Unit Operations of Chemical Engineering, McCabe, W.L. and Smith, J.C., McGraw Hill, 1976, p 159 to 168 and p. 771 to 799. An alternate embodiment applicable to the present development would be to evaporate the 8-Nonenal with a process under vacuum such as a vacuum fluidized bed or a vacuum oven system.

An alternate process for removing 8-Nonenal from starting resin materials, in-process materials such as regrind or from the final package is extraction from the plastic via washing. Water can be used as the solvent and the rate or level of extraction will be dependent upon the water temperature. The water temperature should be between about 150 to about 212°F (65 to 100°C), preferably between about 200 to about 210°F (93 to 99°C). The extraction time should be between about 1 to about 24 hours, preferably between about 2 to about 10 hours and more preferably between about 3 to about 5 hours. The ratio of the weight of water to the weight of the plastic containing material should be between about 10:1 to about 1:1, preferably between about



6:1 to about 3:1. Agitation can be used to improve the extraction efficiency and reduce the time needed to extract the 8-Nonenal. An alternate process would be to complete the extraction under vacuum. Examples of suitable extraction processes applicable to the present development can be found in Unit Operations of Chemical Engineering, McCabe, W.L. and Smith, J.C., McGraw Hill, 1976, p. 607-641 or in the Chemical Engineers Handbook, Perry, R.H. and Chilton, C.H., McGraw Hill, 5<sup>th</sup> ed., 1973, p. 21-4 to 21-29.

Plastics containers can be composed of a monolayer of plastic material including but not limited to ethylenes, nylons, styrenes, polyesters, vinyl chlorides, vinyl alcohols, and polyacrylonitriles. Preferred package mono-layer thickness varies depending on the package performance requirements and uses. Preferably monolayer plastic package thickness is from about 0.001 to about 0.375 inch depending on application requirements. For example, microwavable or storage packages which need higher strength because the contents and such the absolute strength requirements are undefined versus a package designed to hold a specific product such as a bag to hold potato chips is much thinner because the strength requirements are known. However said monolayer plastic containers often have relatively high gas permeability and/or relatively high water permeability and/or relatively high chemical permeability and/or are relatively high cost. Hence they are either insufficient in that the contents cannot be preserved with safety for a relatively long time without deterioration or degradation of contents or are cost prohibitive in maintaining a competitive package price. For example, polyolefins most broadly used for these plastic containers, such as polyethylene, are excellent in moisture barrier properties, water impermeability and sanitary characteristics, but they have a high oxygen permeability and hence they are not suitable for uses where the contents such as foods or beverages are preserved and stored for a long time.

Barrier materials are those that limit the transport of foreign molecules through their structure. A materials barrier property can be defined by its permeability which is a function of resistance to diffusion and sorption of the foreign molecule by the material. High-barrier materials have low solubility (S) and diffusion (D) coefficients. Several factors influence a polymers barrier capability including (1) degree of crystallinity, (2) chemical composition, (3) presence of additives, (4) temperature, and (5) glass-transition temperature. As a polymer morphology changes from amorphous to crystalline, the polymer matrix increases in density and provides a more tortuous diffusion path. Polymer chain chemistry such as polarity can affect permeability by increasing the packing efficiency of the chain and bonding to polar foreign materials. When soluble additives such as but not limited to plasticizers are present in the plastic

diffusion increases because the polymer chains pack density decreases. Temperature increases diffusion while decreasing solubility. Polymers below their glass-transition temperature ( $T_g$ ) have a higher density than when above said temperature. As such, there is a greater permeability change per degree temperature above  $T_g$  than below  $T_g$ .

Polarity and size of the foreign molecules affect the rate of diffusion through polymer materials. Barrier materials are often used to prevent the migration of both small and large molecules including but not limited to nitrogen, oxygen, water, ethyl hexanoate, hexanol, 3-octanone, and d-Limonene. Permeability of larger permeant such as flavor and aroma molecules is inversely proportional to molecular weight. Preferred permeability of flavors and aromas through barrier polymers is less than about 1000 nmol/m s Gpa, more preferably less than about 500 nmol/m s Gpa, still more preferably less than about 100 nmol/m s Gpa, and most preferably less than about 10 nmol/m s Gpa. Preferably the barrier layer is impermeable to foreign flavors and aromas that have a molecular weight between about 40 to about 230 g/mol, more preferably between about 80 to about 200 g/mol, still more preferably between about 100 to about 180 g/mol, and most preferably between about 130 to about 150 g/mol.

Accordingly, to improve package barrier properties a laminate structure can be employed. This laminate structure can then utilize a single or plurality of barrier materials including but not limited to ethylene vinyl alcohol copolymer, polyvinylidene chloride copolymers (SARAN), ethylene vinyl alcohol, polyvinyl chloride (PVDC), acrylonitrile methylacrylate copolymer, poly-chlorotrifluoroethylene, aromatic polyamide, amorphous polyamide, metalized polymers, glass coatings, ceramic coatings, amorphous carbon coatings, nylon, aluminum, and metal alloys. Preferably, the barrier layer would be toward the inside of the package structure separating the product from any package materials that have elevated 8-Nonenal levels. The barrier layer can be the first layer on the inside of the package, adjacent to the product. An alternate embodiment would be to have a minimal substrate layer preceding a barrier layer where the barrier layer separates the product from the bulk of the package 8-Nonenal content. The minimal substrate layer should have a low 8-Nonenal concentration between about 0 to about 1000 ppt, preferably between about 0 to about 500 ppt, and more preferably between about 0 to about 300 ppt. The minimal substrate layer can be used to protect the integrity of the barrier layer. These structures would minimize the packages transfer of 8-Nonenal to the product. Substrate layers can be comprised of a combination of materials including but not limited to virgin material, additives, and recycled material. In some instances it is desirable to keep a separate recycle layer where this layer is comprised of recycle material,

additives, and virgin material. The barrier layer or layers are bonded to the substrate chemically or through the use of an adhesive tie layer. One embodiment, a two layer structure where the barrier layer is bonded directly to the substrate is illustrated in Figure 2. Figure 3 illustrates another embodiment where the barrier layer utilizes an adhesive tie layer to form the bond to the substrate. Figures 4 and 5 show another embodiment where the barrier layer is protected from degradation by an interior layer of either the same or a different substrate than is on the outside of the barrier layer. Figure 6 illustrates a layer sequencing that utilizes a recycle layer and two tie layers to bond the barrier layer to the adjacent layers.

The disclosures of all patents, patent applications (and any patents which issue thereon, as well as any corresponding published foreign patent applications), and publications mentioned throughout this patent application are hereby incorporated by reference herein. It is expressly not admitted, however, that any of the documents incorporated by reference herein teach or disclose the present invention. It is also expressly not admitted that any of the commercially available materials or products described herein teach or disclose the present invention.

### **Analytical Methods**

#### **References**

Schultz, T.H., Fath, R.A., Mon, T.R., Egging, S.B., and Teranishi, R. "Isolation of Volatile Compounds" J. Agric. Food Chem., Vol. 25, No. 3, May-June (1977) pp. 446-449.

#### **Sample Preparation**

Food products should be cut, ground or chopped to small pieces with a characteristic length of about 1/8 inch and a thickness between about 0.03 to about 0.07 inches. A food processor, mortar and pestle, or compression through a funnel can be used to achieve the desired particle size.

The rigid and semi-rigid plastic materials should be reduced to a fine, granular powder that will flow through a number 12 U.S. Sieve Size (1680 microns). The procedure for grinding the rigid or semi-rigid plastic materials is to first cut the material into small pieces with a characteristic dimension between about 1/8 to 3/8 inches, then cool the material with dry ice for about 10 minutes where the ratio of dry ice to plastic is about 10:1 to about 4:1. The plastic and dry ice are intimately mixed. After cooling the material can be ground using a Model RT commercial food processor made by Robot Coupe corporation of Ridgeland, Miss.. Alternately, any comminutive type grinding device with a tight blade tolerance can be used to grind the plastic.

### Extraction

A 30 g sample is steam distilled at atmospheric pressure and the distillate is methylene chloride-extracted at the same time. The apparatus and general procedure is described in the reference above. In the current application of this procedure, 150 g of cis-6-nonenal (internal standard) is added to the 30 g ground sample prior to distillation/extraction. To the sample and internal standard is added 700 mL of distilled, de-ionized water. Distillation/extraction is carried out for 90 minutes using 100 mL methylene chloride as the extracting solvent. The methylene chloride extract is concentrated to 300  $\mu$ L (plastic materials) or 100  $\mu$ L (food products) under a gentle stream of nitrogen.

### 2-D GC/MS Measurement of 8-nonenal Levels in Product and Package Extracts

The methylene chloride extract from simultaneous distillation/extraction is injected into the injection port of a Siemens Sicchromat 2-8 gas chromatograph operated in the 2-dimensional mode using splitless injection. GC conditions:

Column 1	30 M x 0.32 mm, 1.0 $\mu$ film thickness, DB-1701*
Column 2	30 M x 0.32 mm, 0.25 $\mu$ film thickness, DB-5*
Injector Temperature	225°C
Oven 1	40°C (5 min hold) to 225°C at 7°C/min
Oven 2	40°C (25.5 min hold) to 225°C at 2°C/min
Heart cut	From 25.2 min to 25.8 min
Injection volume	1 $\mu$ L

\*J&W Scientific

Both 8-nonenal and the internal standard (cis-6-nonenal) elute between 25.2 min and 25.8 min on the first column, and are diverted onto the 2<sup>nd</sup> column. The heart cutting operation is done manually based on the appearance of the chromatogram as monitored by a flame ionization detector connected via "live-T" to column 1, so the heart cutting times may vary slightly. Detection of the effluent from column 2 is done using high resolution mass spectrometry with a Finnigan MAT95 Q operated in selected ion monitoring mode. Mass spectrometry conditions:

Ionization	electron ionization (70 eV)
Resolution (10% valley)	3000
Lock mass	perfluorokerosene, m/z 99.9936
Quantitation masses	98.0732, 81.0704
Dwell times	202 msec (m/z 98,81), 19.11 msec (m/z 100)

For plastic and food samples,  $m/z$  98 at column 2 retention time ( $RT_2$ ) = 23.6 min is used to measure the internal standard. For plastic samples,  $m/z$  98 is also used to measure 8-nonenal at  $RT_2$  = 23.2 min. For food samples,  $m/z$  81 is used to measure 8-nonenal at  $RT_2$  = 23.2 min, as this  $m/z$  is less susceptible to interferences.

WHAT IS CLAIMED IS: